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(54) Process for converting olefins into higher hydrocarbons.

(57) In the conversion of olefins into higher hydrocarbons, a feedstock comprising ethylene and C_3^+ olefins is prefractionated to obtain gaseous ethylene and a liquid stream containing C_3^+ olefins; the C_3^+ olefins are then oligomerized to obtain distillate and gasoline fractions and part of the gasoline fraction is recycled and used as the prefractionation sorbent.

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PROCESS FOR CONVERTING OLEFINS INTO HIGHER HYDROCARBONS

This invention relates to a process for converting olefins into higher hydrocarbons, for example gasoline boiling-range and distillate boiling-range fuels.

Improved catalytic hydrocarbon conversion processes have created interest in utilizing olefinic feedstocks, such as petroleum refinery streams rich in lower olefins, for producing C_5^+ gasoline and diesel fuel, for example. In addition to the basic work derived from ZSM-5 type zeolite catalyst research, a number of discoveries have contributed to the development of new industrial processes, such as that known as the Mobil Olefins-to-Gasoline/Distillate (MOGD) process. This process has significance as a safe, environmentally acceptable technique for utilizing refinery streams that contain lower olefins, especially C_2-C_5 alkenes, and may supplant conventional alkylation units. U.S. Patents 3,960,978 and 4,021,502 describe the conversion of C_2-C_5 olefins, alone or in admixture with paraffinic components, into higher hydrocarbons over crystalline zeolites having controlled acidity. Improved processing techniques relevant to the MOGD system are described in U.S. Patents 4,150,062, 4,211,640 and 4,227,992.

The conversion of lower olefins, especially propene and butenes, over H-ZSM-5 is effective at moderately elevated temperatures and pressures. The conversion products are sought as liquid fuels, especially the C_5^+ aliphatic and aromatic hydrocarbons. Olefinic gasoline is produced in good yield by the MOGD process and may be recovered as a useful product or recycled to the reactor system for further conversion into distillate boiling-range products.

As a consequence of the relatively low reactivity of ethylene with known zeolite oligomerization catalysts (about 10-20%

conversion for HZSM-5), distillate-mode reactor systems designed completely to convert a large ethylenic component of feedstock would require a much larger size than comparable reactor systems for converting other lower olefins. Recycle of a major amount of ethylene from the reactor effluent would result in significant increases in equipment size. By contrast, propene and butene are converted efficiently, 75 to 95% or more in a single pass, under catalytic conditions of high pressure and moderate temperature used in distillate mode operations.

The present invention is based on the observation that an olefins-to-distillate process using a C_2-C_4 olefinic feedstock can be combined with a feedstock prefractionating step; in this manner, the C_3^+ olefinic components can be catalytically converted into a distillate boiling-range product and ethylene can be recovered economically for use in polymer manufacture or in other industrial processes.

According to the invention, there is provided a process for converting an olefinic feedstock comprising ethylene and C_3^+ olefins into a heavier liquid hydrocarbon product, comprising the steps of:

(a) prefractionating the olefinic feedstock to obtain a gaseous stream rich in ethylene and a liquid stream containing C_3^+ olefins;

(b) vaporizing the liquid stream from step (a) and contacting the vapor with an oligomerization catalyst in at least one exothermic reaction zone to provide a heavier hydrocarbon effluent stream comprising distillate, gasoline and lighter hydrocarbons;

(c) cooling and fractionating the effluent stream from step (b) separately to recover distillate, gasoline and lighter hydrocarbons; and,

(d) recycling at least a portion of the gasoline recovered in step (c) as a liquid sorbent stream to prefractionating step (a).

According to a preferred aspect of the invention, the process includes an additional step of (e) passing the hot effluent from the exothermic reaction zone in step (b) in indirect heat exchange in a reboiler loop with at least a portion of the liquid stream containing C_3^+ olefins in prefractionating step (a).

The prefractionation step (a) of the process, which is described in greater detail below, separately forms the subject of copending application (applicant's reference F-2299-L).

The olefinic feedstock for the process of the invention may be obtained from various sources, including fossil fuel processing streams, such as gas separation units, cracking of C_2^+ hydrocarbons, coal byproducts, alcohol conversion, and various synthetic fuel processing streams. Olefinic effluent from fluidized catalytic cracking of gas oil, for example, is a valuable source of olefins, mainly C_3-C_4 olefins, suitable for exothermic conversion by the MOGD process.

Typically, the olefinic feedstock consists essentially of C_2-C_6 aliphatic hydrocarbons containing a major fraction of monoalkenes in the essential absence of dienes and other deleterious materials. The process may employ various volatile lower olefins as feedstock, with oligomerization of C_3^+ alpha-olefins being preferred for either gasoline or distillate production. Preferably the olefinic feedstock contains from 50 to 75 mole % C_3-C_5 alkenes.

The reactions involved in the olefins-to-distillate process are preferably carried out in the presence of medium pore silicaceous metal oxide crystalline catalysts, such as acid ZSM-5 type zeolites catalysts. These materials are commonly referred to as aluminosilicates or porotectosilicates; however, the acid function may be provided by other tetrahedrally coordinated metal oxide moieties, especially Ga, B, Fe and Cr. Commercially available aluminosilicates such as ZSM-5 are preferably employed in the operative embodiments; however, it is to be understood that other silicaceous catalysts having similar pore sizes and acidic functions may also be used.

The catalyst materials especially suitable for use in the process of the invention are effective in oligomerizing lower olefins, especially propene and butene-1 into higher hydrocarbons. The unique characteristics of the acid ZSM-5 catalyts are particularly suitable for use in the MOGD system. An especially preferred catalyst material for use in the process is an extrudate (1.5mm) comprising 65 weight % HZSM-5 and 35% alumina binder, having an acid cracking activity (α) of about 160 to 200.

The members of the class of crystalline zeolites that may be used in the process of the invention are characterized by a pore dimension greater than about 5 Angstroms (0.5nm); i.e., they are capable of sorbing paraffins having a single methyl branch as well as normal paraffins, and they have silica to alumina mole ratios of at least 12. Although such crystalline zeolites with a silica to alumina mole ratio of at least about 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. In some zeolites, the upper limit of silica to alumina mole ratio is virtually unbounded; i.e., values of 30,000 and greater.

The members of this class of zeolites are exemplified by ZSM-5, ZSM-5/ZSM-11 intermediate, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and other similar materials. These zeolites are described in, for example, U.S. Patents 3,702,886; Re. No. 29,948; 4,061,724; 4,229,424; 3,709,979; 3,832,449; 4,076,842; 4,016,245; and 4,046,859; and EP-A-13640.

The zeolites used in additive catalysts may be in hydrogen form or they may be base exchanged or impregnated to contain a rare earth cation complement. Such rare earth cations comprise Sm, Nd, Pr, Ce and La. It is desirable to calcine the zeolite after base exchange.

The catalyst and separate additive composition may be prepared in various ways. They may be separately prepared in the form of particles such as pellets or extrudates, for example, and simply mixed in the required proportions. The particle size of the individual component particles may be quite small, for example from about 10 to about 150 µm, when intended for use in fluid bed operation, or they may be as large as 1-10 mm for fixed bed operation. Alternatively, the components may be mixed as powders and formed into pellets or extrudate, each pellet containing both components in substantially the required proportions. It is desirable to incorporate the zeolite component of the separate additive composition in a matrix. Such matrix is useful as a binder and imparts greater resistance to the catalyst to the severe temperature, pressure and velocity conditions encountered in many cracking processes. Matrix materials include both synthetic and natural substances; for example, clays, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Frequently, zeolite materials have been incorporated into naturally occurring clays; for example, bentonite and kaolin.

A particularly advantageous form of the catalyst is an extruded pellet having a diameter of about 1-3mm, made by mixing steamed zeolite crystals (for example silica:alumina = 70:1 - 500:1) with α-alumina monohydrate in a proportion of about 2:1 and calcining the resulting mixture to obtain an extrudate having a void fraction of about 30-40%, preferably about 36%.

The process of the invention is described below in greater detail by way of example only with reference to the accompanying drawings, in which:

FIGURE 1 is a simplified flow diagram showing the relationship of the major units of the process;

FIGURE 2 is a more detailed flow diagram of the process; and,

FIGURE 3 is a flow diagram of the prefractionation step of the process.

Referring to the drawings, the overall relationship of the invention to a petroleum refinery is depicted in FIG. 1. Various olefinic and paraffinic light hydrocarbon streams may be involved in the reactor or fractionation subsystems. An olefinic feedstock, such as C_2-C_4 olefins derived from catalytic cracker (FCC) effluent, may be employed as a feedstock rich in ethene, propene, and butenes for the process. The prefractionator/absorber unit separates the feedstock into a relatively pure ethene gas product and C_3^+ liquid comprising the rich sorbent. Following reaction at elevated temperature and pressure over a shape selective catalyst, such as ZSM-5, the reactor system effluent is fractionated. The fractionation sub-system has been devised to yield three main liquid product streams - LPG (mainly C_3-C_4 alkanes), gasoline boiling range hydrocarbons (C_5 to 165°C) and distillate range heavier hydrocarbons (165°C$^+$). Optionally, all or a portion of the olefinic gasoline range hydrocarbons from the product fractionator unit may be recycled for further conversion to heavier hydrocarbons in the distillate range. This may be accomplished by combining the recycle gasoline with C_5^+ olefin feedstock in the prefractionation step prior to heating the combined streams.

Process conditions, catalysts and equipment suitable for use in the MOGD process are described in U.S. Patents 3,960,978, 4,021,502 and 4,150,062. Hydrotreating and recycle of olefinic gasoline are described in U.S. Patent 4,211,640. Other pertinent disclosures include U.S. Patent 4,227,992 and U.S. Patent Application 488,834, relating to catalytic processes for converting olefins to gasoline/distillate.

Referring to FIG. 2, olefinic feedstock is supplied to the plant through a fluid conduit 1 under steady stream conditions. The olefins are separated in a prefractionator 2 to recover an ethylene-rich stream 2E and a liquid hydrocarbon stream 2L containing C_3^+ feedstock components, as described in detail below. This C_3^+ feedstream is pressurized by a pump 12 and then sequentially heated by passing through indirect heat exchange units 14 and 16 and furnace 20 to achieve the temperature for catalytic conversion in reactor system 30, including reactor vessels 31A, 31B, 31C, etc.

The reactor system section shown consists of 3 downflow fixed bed, series reactors on line with exchanger cooling between reactors. The reactor configuration allows for any reactor to be in any position, A, B or C. The reactor in position A has the most aged catalyst and the reactor in position C has freshly regenerated catalyst. The cooled reactor effluent is fractionated first in a debutanizer 40 to provide lower aliphatic liquid recycle and then in splitter unit 50 which not only separates the debutanizer bottoms into gasoline and distillate products but also provides liquid gasoline recycle.

The gasoline recycle is necessary not only to produce the proper distillate quality but also to limit the exothermic rise in temperature across each reactor to less than 30°C. Change in recycle flow rate is intended primarily to compensate for gross changes in the feed non-olefin flow rate. As a result of preheat, the liquid recycle is substantially vaporized by the time that it reaches the reactor inlet. The following is a description of the process flow in detail.

Sorbed C_3^+ olefin combined with olefinic gasoline is pumped up to system pressure by pump 12 and is combined with gasoline recycle after that stream has been pumped up to system pressure by a pump 58. The combined stream (C_3^+ feed plus gasoline recycle) after preheat is routed to inlet 30F of reactor 31A of system 30. The combined stream (designated as the reactor feedstream) is first preheated against the splitter tower 50 effluent in exchanger 14 (reactor feed/splitter tower bottoms exchanger) and then against the effluent from the reactor in position C, in exchanger 16 (reactor feed/reactor effluent exchanger). In the furnace 20, the reactor feed is heated to the required inlet temperature for the reactor in position A.

Because the reaction is exothermic, the effluents from the reactors in the first two positions, A and B, are cooled to the temperature required at the inlet of the reactors in the last two positions, B and C, by partially reboiling the debutanizer 40. Temperature control is accomplished by allowing part of the reactor effluents to bypass the reboiler 42. Under temperature control of the bottom stage of the sorption fractionator 2, energy for reboiling is provided by at least part of the effluent from the reactor 31 in position C.

After heating fractionator 2 reboiler, the reactor effluent reboils deethanizer bottoms 61 and is then routed to the debutanizer 40 which is operated at a pressure which completely condenses the debutanizer tower overhead 40V by cooling in condenser 44. The liquid from debutanizer overhead accumulator 46 provides the tower reflux 47, and feed to the deethanizer 60, which, after being pumped to deethanizer pressure by pump 49 is sent to the deethanizer 60. The deethanizer accumulator overhead 65 is routed to the fuel gas system. The accumulator liquid 64 provides the tower reflux. The bottoms stream 63 (LPG product) may be sent to an unsaturated gas plant or otherwise recovered.

The bottoms stream 41 from the debutanizer 40 is sent directly to the splitter, 50 which splits the C_5^+ material into C_5-165°C gasoline (overhead liquid product and recycle) and 165°C$^+$ distillate (bottoms product). The splitter tower overhead stream 52 is totally condensed in the splitter tower overhead condenser 54. The liquid from the overhead accumulator 56 provides the tower reflux 50L, the gasoline product 50P and the specified gasoline recycle 50R under flow control, pressurized by pump 58 for recycle. After being cooled in the gasoline product cooler 59, the gasoline product is sent to the gasoline pool. The splitter bottoms fraction is pumped to the required pressure by pump 58 and then preheats the reactor feed stream in exchanger 14. Finally, the distillate product 50D is cooled to ambient temperature before being hydrotreated to improve its cetane number.

From an energy conservation standpoint, it is advantageous to reboil the debutanizer 40 using reactor effluent as opposed to using a fired reboiler. A kettle reboiler 42 containing 2 U-tube exchangers 43 in which the reactor 31 effluents are circulated is a desirable feature of the system. Liquid from the bottom stage of debutanizer 40 is circulated in the shell side.

The thermal integration techniques employed in the system depicted in Fig. 2 provide flexible process conditions for startup and steady state operation of MOGD feedstock and effluent fractionation subsystems. After preheating the reactor feed, the reaction section effluent reboils prefractionation liquid bottoms and the deethanizer before mixing with the sponge absorber bottoms and entering the debutanizer. Prefractionated olefinic feedstock is fed to the reactor after receiving some preheat from the distillate product stream and, depending on the third reactor effluent temperature, the reactor feedstock may also receive preheat from the reactor effluent before entering the furnace, where it is heated to the temperature required for the reactor in initial position A.

The effluents from the first two reactors are cooled to the inlet temperatures for the last two reactors by reboiling the debutanizer and product splitter. Reactor inlet temperature control is achieved by regulating the amount of first reactor effluent sent to the gasoline/distillate splitter reboiler and the amount of intermediate reactor effluent sent to the debutanizer reboiler. The amount of first reactor effluent sent to the debutanizer reboiler is temperature controlled by the debutanizer bottom stage temperature. If needed, a portion of the first reactor effluent sent to the product splitter may be routed through the furnace convection section for auxiliary heating.

In order to provide the desired quality and rate for gasoline recycle, it is necessary to fractionate the reactor effluent. Phase separators do not give the proper separation of the reactor effluent to meet the quality standards and rate for both liquid recycles. For example, the gasoline recycle would carry too much distillate and lights. Consequently, it would be difficult to properly control the liquid recycle if separators were employed.

The product fractionation units 40, 50, and 60 may be a tray-type design or packed column. The splitter distillation tower 50 is preferably operated at substantially atmospheric pressure to avoid excessive bottoms temperature, which might be deleterious to the distillate product. The fractionation equipment and operating techniques are substantially similar for each of the major stills 40, 50, 60, with conventional plate design, reflux and reboiler components. The fractionation sequence and heat exchange features of the present system are operatively connected in an efficient MOGD system provide significant economic advantages.

MOGD operating modes may be selected to provide maximum distillate product by gasoline recycle and optimal reactor system conditions. Operating examples are given for distillate mode operation, utilizing as the olefinic feedstock a pressurized stream olefinic feedstock (about 1200 kPa) comprising a major weight and mole fraction of $C_3^=/C_4^=$. The adiabatic exothermic oligomerization reaction conditions are readily optimized at elevated temperature and/or pressure to increase distillate yield or gasoline yield as desired, using HZSM-5 type catalyst. Particular process parameters such as space velocity and maximum exothermic temperature rise may be optimized for the specific oligomerization catalyst employed, olefinic feedstock and desired product distribution.

A typical distillate mode multi-zone reactor system employs inter-zone cooling, whereby the reaction exotherm can be carefully controlled to prevent excessive temperature above the normal moderate range of about 190° to 315°C.

Advantageously, the maximum temperature differential (ΔT) across any one reactor is about 30°C and the space velocity (LHSV based on olefin feed) is about 0.5 to 1. Heat exchangers provide inter-reactor cooling and reduce the effluent to fractionation temperature. It is an important aspect of energy conservation in the MOGD system to utilize at least a portion of the reactor exotherm heat value by exchanging hot reactor effluent from one or more reactors with a fractionator stream to vaporize a liquid hydrocarbon distillation tower stream, such as the debutanizer reboiler. Optional heat exchangers may recover heat from the effluent stream prior to fractionation. Gasoline from the recycle conduit is pressurized by a pump and combined with feedstock, preferably at a mole ratio of about 1-2 moles per mole of olefin in the feedstock. It is preferred to operate in the distillate mode at elevated pressure of about 4200 to 7000 kPa.

The reactor system contains multiple downflow adiabatic catalytic zones in each reactor vessel. The liquid hourly space velocity (based on total fresh feedstock) is about 1 LHSV. In the distillate mode the inlet pressure to the first reactor is about 4200 kPa, with an olefin partial pressure of at least about 1200 kPa. Based on olefin conversion of 50% for ethene, 95% for propene, 85% for butene-1 and 75% for pentene-1, and exothermic heat of reaction is estimated at 1050 kJ/kg of olefins converted. When released uniformly over the reactor beds, a maximum ΔT in each reactor is about 30°C. In the distilate mode the molar recycle ratio for gasoline is equimolar based on olefins in the feedstock, and the C_3-C_4 molar recycle is 0.5:1.

The prefractionation system is adapted to separate volatile hydrocarbons comprising a major amount of C_2-C_4' olefins, and typically contains 10 to 50 mole % of ethene and propene each. In the detailed examples below the feedstock consists essentially of volatile aliphatic components as follows (in mole %): ethene, 24.5%; propene, 46%; propane, 6.5%; 1-butene, 15%; and butanes, 8%, having an average molecular weight of about 42 and more than 85% olefins.

The gasoline sorbent is an aliphatic hydrocarbon mixture boiling in the normal gasoline range of about 50 to 165°C, with minor amounts of C_4-C_5 alkanes and alkenes. Preferably, the total gasoline sorbent stream to feedstock weight ratio is greater than about 3:1; however, the content of C_3^+ olefinic components in the feedstock is a more preferred measure of sorbate to sorbent ratio. Accordingly, the process may be operated with a mole ratio of about 0.2 moles to about 10 moles of gasoline per mole of C_3^+ hydrocarbons in the feedstock, with optimum operation utilizing a sorbent:sorbate molar ratio about 1:1 to 1.5:1.

Referring to Fig.3, olefinic feedstock is introduced to the system through a feedstock inlet 1 connected between stages of a fractionating sorption tower 2 in which gaseous olefinic feedstock is contacted with liquid sorbent in a vertical fractionation column operating at least in the upper portion thereof in countercurrent flow. Effectively this unit is a C_2/C_3^+ splitter. Design of sorption equipment and unit operations are established chemical engineering techniques, and generally described in Kirk-Othmer "Encyclopedia of Chemical Technology" 3rd Ed. Vol. 1 pp. 53-96 (1978). In conventional refinery terminology, the sorbent stream is sometimes known as lean oil.

Sorption tower 2, as depicted, has multiple contact zones, with the heat of absorption being removed via interstage pumps around cooling circuits 2A, 2B. The liquid gasoline sorbent is introduced to the sorption tower through an upper inlet 2C above the top contact section 2D. It is preferred to mix incoming liquid sorbent with outgoing splitter overhead ethylene-rich gas from upper gas outlet 2E and to pass this multi-phase mixture into a phase separator 2F, operatively connected between the primary sorption tower 2 and a secondary sponge absorber 3. Liquid sorbent from separator 2F is then pumped to the upper liquid inlet 2C for countercurrent contact in a plate column or the like with upwardly flowing ethylene-rich vapors. Liquid from the bottom of upper contact zone 2D is pumped to a heat exchanger in loop 2A, cooled and returned to the tower above intermediate contact zone 2G, again cooled in loop 2B, and returned to the tower above contact zone 2H, which is located below the feedstock inlet 1. Under tower design conditions of about 2100 kPa, it is preferred to maintain the liquid temperature of streams entering the tower from 2A, 2B and 2F at about 40°C. The lower contact zone 2H provides further fractionation of the olefin-rich liquid. Heat is supplied to the sorption tower by removing liquid from the bottom via reboiler loop 2J, heating this stream in heat exchanger 2K, and returning the reboiled bottom stream to the tower below contact zone 2H.

The liquid sorbate-sorbent mixture is withdrawn through bottom outlet 2L and used as feedstock in the olefins oligomerization unit. Ethylene rich vapor from the primary sorption tower is withdrawn via separator 2F through conduit 3A.

Distillate lean oil is fed to the top inlet 3B of sponge absorber 3 under process pressure at ambient or moderately warm temperature (for example 40°C) and distributed at the top of a porous packed bed, such as Raschig rings, having sufficient bed height to provide multiple stages. The liquid rate is low; however, the sponge absorber permits sorption of about 25 weight percent of the distillate weight in C_3^+ components sorbed from the ethylene-rich stream. This stream is recovered from bottom outlet 3C. It is understood that the sorbate may be recovered from the mixture with the sorbent by fractionation and the sorbent may be recycled or otherwise utilized. High purity ethylene is recovered from the system through gas outlet 3D and sent to storage, further processing or conversion to other products.

The sorption towers depicted in the drawing employ a plate column in the primary tower and a packed column in the secondary tower, however, the fractionation equipment may employ vapor-liquid contact means of various designs in each stage including packed beds of Raschig rings, saddles or other porous solids or low pressure drop valve trays (Glitsch grids). The number of theoretical stages will be determined by the feedstream composition, liquid:vapor (L/V) ratios, desired recovery and product purity. In the detailed example below, 17 theoretical stages are employed in the primary sorption tower and 8 stages in the sponge absorber, with olefinic feedstock being fed between the 7th and 9th stages of the primary sorption tower.

The following Examples illustrate the invention. They are based on the feedstock described above at 40°C and 2100 kPa supplied to stage 9 of the primary sorption tower. Gasoline is supplied at 85°C and 2150 kPa, and distillate lean oil is supplied at 40°C and 2100 kPa. Table I shows the conditions at each stage of the primary sorption tower, and Table II shows the conditions for the sponge absorber units for Example 1 (2 moles gasoline/mole of olefin in feedstock).

TABLE I

Stage	Heat In (KW/tonne)	Temperature (°C)	Liquid/Vapor (L/V) Mole Ratio	Pressure (kPa)
1 (top)	-121. + 362(1)	37.8	6.947	2068.5
2		38.5	2.245	2103.0
3		39.7	2.222	2103.7
4		42.3	2.227	2104.4
5		47.2	2.221	2105.1
6		54.2	2.185	2105.8
7	-29.(2)	57.6	2.216	2106.5
8		65.3	1.864	2107.2
9	-820. + 120(3)	59.9	2.447	2107.9
10		67.7	1.954	2108.6
11		71.8	1.814	2109.3
12		74.1	1.743	2110.0
13		75.4	1.704	2110.7
14		77.0	1.684	2111.4
15		80.5	1.644	2112.1
16		92.3	1.541	2112.8
17(bottom)	400.(4)	136.2	0.872	2116.3

(1) Condenser Duty & Lean Oil

(2) 1st Heat Removal Duty

(3) 2nd Heat Removal Duty & Lean Oil

(4) Reboiler Duty, based on tonnes of feedstock

TABLE II

Stage	Heat In (KW/tonne)	Temperature (°C)	Liquid/Vapor (L/V) Mole Ratio	Pressure (kPa)
1	2.9(1)	42.8	0.045	1999.6
2		42.3	0.046	2000.2
3		41.8	0.046	2000.9
4		41.4	0.047	2001.6
5		41.2	0.047	2002.3
6		40.9	0.048	2003.0
7		40.6	0.050	2003.7
8	32.8(2)	40.1	0.056	2004.4

(1) Distillate Lean Oil

(2) $C_2^{=}/C_3^{=+}$ Splitter Overhead

Examples 1 to 9

Based on the above design, the following data show the effects of varying the flow rate of gasoline absorbent in the primary tower C_2/C_3^{+} splitter overhead and the corresponding effects of varying the distillate lean oil rate in the secondary sponge absorber. These data are shown in Table III, which give the ethylene ($C_2^{=}$) recovery and purity from each of the primary and secondary sorption units.

TABLE III

Example No.	Gasoline Mole Ratio (1)	Distillate Mole Ratio	$C2/C3^{+}$ Splitter Overhead $C2^{=}$ Recovery %	$C2/C3^{+}$ Splitter Overhead $C2^{=}$ Purity MOL%	$C2/C3^{+}$ Splitter Overhead $C2^{=}$ Purity WT%	Sponge Absorber Overhead $C2^{=}$ Recovery %	Sponge Absorber Overhead $C2^{=}$ Purity MOL%	Sponge Absorber Overhead $C2^{=}$ Purity WT%
1	2:1	0.013	99.92	98.21	95.24	98.37	99.18	97.91
2	1:1	0.013	99.94	85.16	77.74	98.32	86.43	78.39
3	1.5:1	0.013	99.93	96.43	92.56	98.37	97.45	95.53
4	3:1	0.013	99.90	98.40	95.46	98.35	99.36	98.16
5	4:1	0.013	99.88	98.42	95.45	98.32	99.39	98.40
6	2:1	0.006	99.92	98.21	95.24	99.02	98.98	97.48
7	2:1	0.01	99.92	98.21	95.24	98.68	99.09	97.67
8	2:1	0.019	99.92	98.21	95.24	97.77	99.31	98.40
9	2:1	0.025	99.92	98.21	95.24	97.17	99.43	98.65

(1) Gasoline Absorbent Rate Moles/Mole of Total Olefin in Feedstock.

In general, as the flow rate of lean oil increases, the ethylene recovery decreases, while the purity increases. The data for the splitter/absorber combination show that the excellent results are obtained with a gasoline mole ratio of at least 1:1 (based on C_3^+ hydrocarbons). Such conditions will result in a $C_2^=$ recovery of greater than 98%. Purity of more than 99 mole % can be achieved with a gasoline mole ratio of at least 2:1.

The C_3^+ olefin sorbate and gasoline are fed directly to the oligomerization process, with a portion of the recovered gasoline and distillate being recycled to the sorption fractionation system. Table IV shows the boiling range fraction composition for typical gasoline and distillate sorbents.

Table IV

Lean Oil Compositions (MOL %)

	Gasoline	Distillate
Propane	0.00	0
Isobutane	0.15	0
1-Butene	0.12	0
N-Butene	0.59	0
Isopentane	2.60	0
1-Pentene	0.24	0
N-Pentane	0.24	0
52-82°C	11.24	0
82-104°C	22.02	0
104-127°C	23.54	0.02
127-138°C	11.23	0.09
138-149°C	10.47	0.43
149-160°C	8.70	2.00
160-171°C	1.54	2.13
171-182°C	0.92	7.06
182-193°C	0.31	11.16
193-204°C	0.10	14.53
204-216°C	0.01	8.36
216-227°C	0.00	8.56
227-238°C	0	7.56
238-249°C	0	6.50
249-260°C	0	6.00
260-271°C	0	4.30
271-293°C	0	5.10
293-316°C	0	4.13
316-338°C	0	3.24
338-360°C	0	3.17
360-382°C	0	4.63
382-404°C	0	0.91
404-438°C	0	0.11

The sponge absorber may be constructed in a separate unit, as shown, or this operation may be conducted in an integral shell vessel with the main fractionation unit. In the alternative integral design, the rich sponge oil may be recovered from the upper contact zone as a separate stream, or the heavy distillate sorbent may be intermixed downwardly with gasoline sorbent and withdrawn from the bottom of the main fractionation zone.

The stream components of the olefinic feedstock and other main streams of the sorption/prefractionator unit and reactor feedstreams are set forth in Table V, based on parts by weight per 100 parts of feedstock.

TABLE V

Component wt.%	Fresh Feed	Main C_1/C_2 Fract.	Gasoline Recycle	Sponge Absorber Feed	Sorption Reflux	Distillate Sorbent	Ethene Product	Sponge Sorber Bottoms	Reactor Inlet
C_1	-	-	-	-	-	-	-	-	-
$C_2^=$	16.3	50.5	-	16.3	34.2	-	16.0	0.3	-
C_2	-	-	-	-	-	-	-	-	-
$C_3^=$	45.9	0.5	-	0.06	0.4	-	0.05	-	45.9
C_3	6.8	0.02	-	-	0.02	-	-	-	6.8
$i\text{-}C_4$	7.7	0.04	0.3	0.02	0.4	-	0.01	-	8.0
$C_4^=$	20.0	0.03	0.2	0.01	0.2	-	-	-	20.1
$n\text{-}C_4$	3.3	0.12	1.0	0.04	1.0	-	0.03	-	4.2
$i\text{-}C_5$	-	0.3	5.4	0.09	5.6	-	0.06	0.04	5.2
C_5	-	0.6	12.5	0.2	12.8	-	0.1	0.09	12.2
$n\text{-}C_5$	-	0.02	0.5	-	0.5	-	-	-	0.5
50-165°C	-	1.4	270.8	0.4	272.8	0.05	-	0.5	270.7
165°C$^+$	-	-	15.6	-	14.1	3.5	-	3.5	15.6
Stream No.	1	2E	50L	3A	2F liq	3B	3D	3C	30F

More than 98% of ethylene is recovered in the above example from the feedstock, and the gas product requires little additional treatment to raise its purity from 99.2 mol% to polymer grade.

In the refining of petroleum or manufacture of fuels from fossil materials or various sources of hydrocarbonaceous sources, an olefinic mixture is often produced. For instance, in cracking heavier petroleum fractions, such as gas oil, to make gasoline or distillate range products, light gases containing ethene, propene, butene and related aliphatic hydrocarbons are produced. It is known to recover these valuable by-products for use as chemical feedstocks for other processes, such as alkylation, polymerization, oligomerization and LPG fuel. Ethylene is particularly valuable as a basic material in the manufacture of polyethylene and other plastics, and its commercial value is substantially higher as a precursor for the chemical industry than as a fuel component. Accordingly, it is desirable to separate ethylene in high purity for such uses.

A typical byproduct of fluid catalytic cracking (FCC) units is an olefinic stream rich in C_2-C_4 olefins, usually in mixture with lower alkanes. Ethylene can be recovered from such streams by conventional fractionation means, such as cryogenic distillation, to recover the C_2 and C_3^+ fractions; however, the equipment and processing costs are high.

There are several reasons for not converting the ethylene into distillate and gasoline. The high pressure and low space velocity required for any significant conversion (on the order of 75 wt. %) would require a separate reactor train and at least one additional tower. This would substantially increase the capital cost of the unit. Converting the ethylene with the propylene/butylene stream would result in an ethylene conversion of about 20 wt. %. Additionally, the value of polymer grade ethylene may be much higher than the gasoline and distillate which would be produced if the ethylene were to be converted. Finally, there would be difficulty in scheduling the regeneration section to regenerate both the ethylene conversion and propylene/butylene conversion reactors.

CLAIMS:

1. A process for converting an olefinic feedstock comprising ethylene and C_3^+ olefins into a heavier liquid hydrocarbon product, comprising the steps of:

(a) prefractionating the olefinic feedstock to obtain a gaseous stream rich in ethylene and a liquid stream containing C_3^+ olefins;

(b) vaporizing the liquid stream from step (a) and contacting the vapor with an oligomerization catalyst in at least one exothermic reaction zone to provide a heavier hydrocarbon effluent stream comprising distillate, gasoline and lighter hydrocarbons;

(c) cooling and fractionating the effluent stream from step (b) separately to recover distillate, gasoline and lighter hydrocarbons; and,

(d) recycling at least a portion of the gasoline recovered in step (c) as a liquid sorbent stream to prefractionating step (a).

2. A process according to claim 1, including the additional step of:

(e) passing the hot effluent from the exothermic reaction zone in step (b) in indirect heat exchange in a reboiler loop with at least a portion of the liquid stream containing C_3^+ olefins in prefractionating step (a).

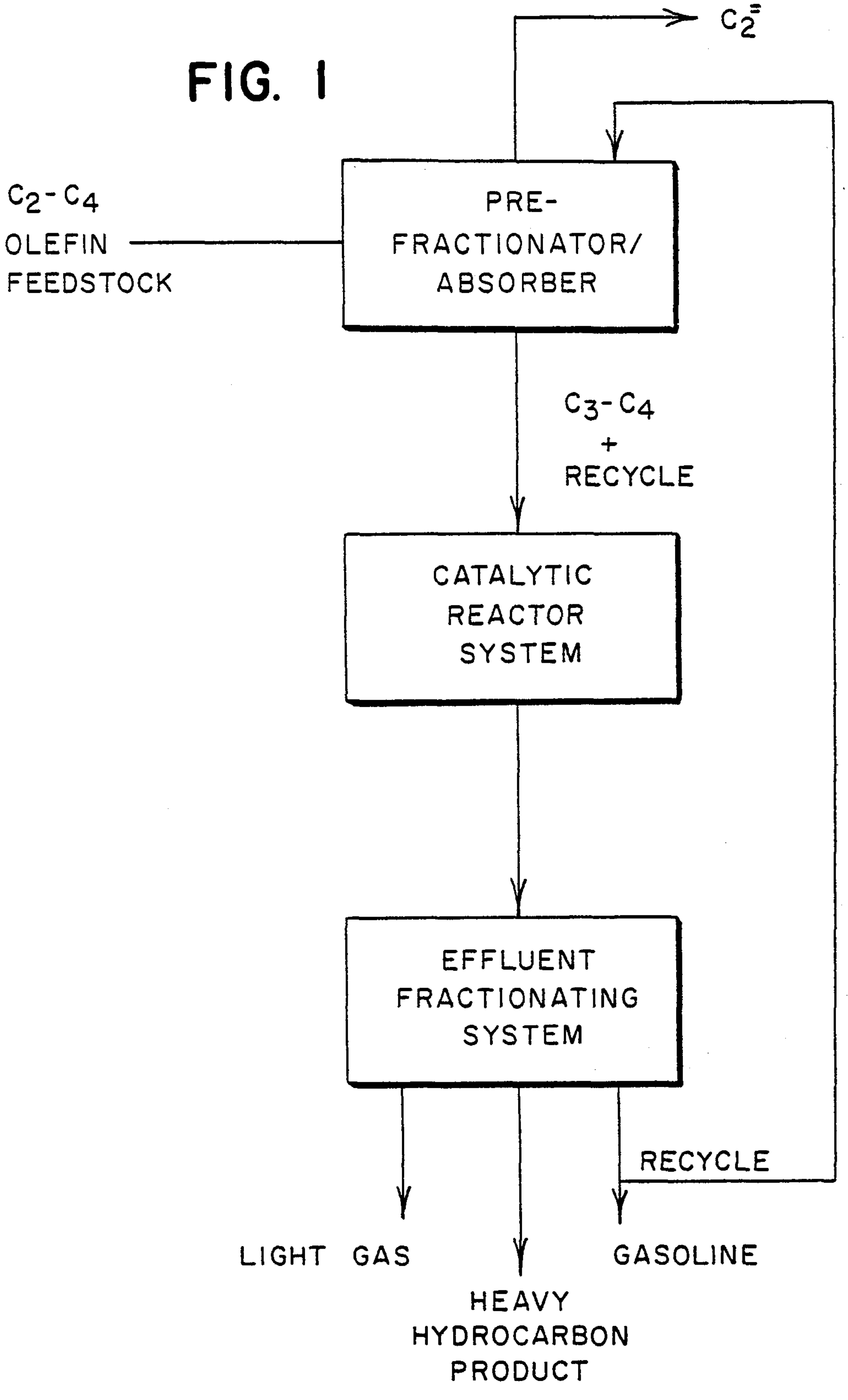
3. A process according to claim 2, wherein the C_3^+ olefins are reacted in step (b) in a series of fixed bed adiabatic reactors at elevated pressure and at a temperature of 190 to 315°C with a maximum temperature rise of about 30°C in each reactor; the effluent from each reactor is cooled prior to entering the next reactor; and the effluent from at least one reactor is heat exchanged with the liquid prefractionation stream to vaporize sorbed hydrocarbons in step (e).

4. A process according to any one of claims 1 to 3, wherein the hot reactor effluent from step (b) contains light gas, olefinic C_5^+ gasoline and distillate boiling-range hydrocarbon components and is fractionated to separate those components in step (c).

5. A process according to any one of claims 2 to 4, wherein following heat exchange with the liquid prefractionation stream, the hot effluent from step (b) is used to reboil a light gas deethanizer.

6. A process according to any one of claims 1 to 5, wherein the oligomerization catalyst comprises acid ZSM-5 type zeolite.

FIG. 1


$C_2^=$
C_2-C_4 OLEFIN FEEDSTOCK
PRE-FRACTIONATOR/ ABSORBER
C_3-C_4 + RECYCLE
CATALYTIC REACTOR SYSTEM
EFFLUENT FRACTIONATING SYSTEM
RECYCLE
LIGHT GAS
HEAVY HYDROCARBON PRODUCT
GASOLINE

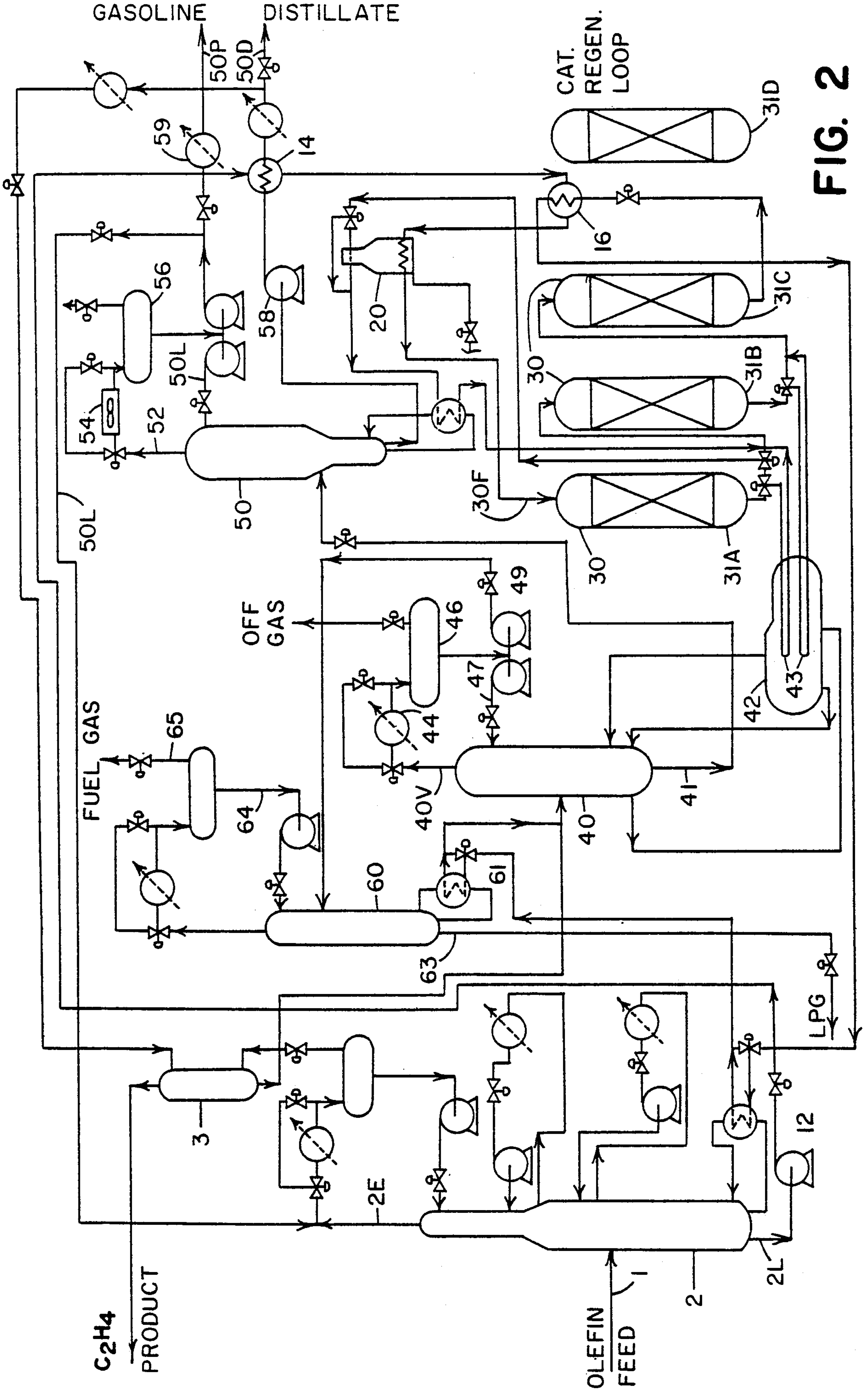
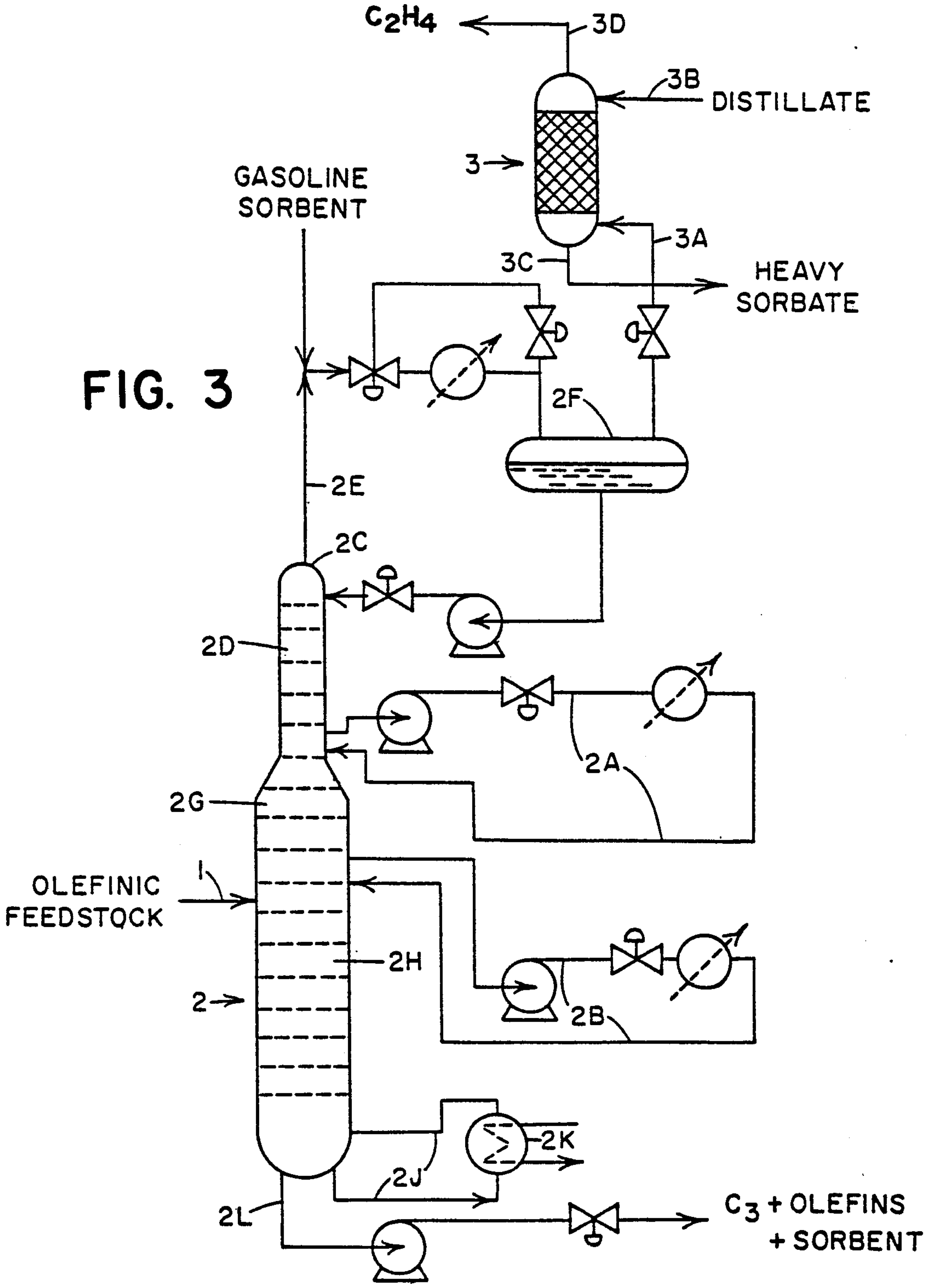

GASOLINE
DISTILLATE
50P
50D
59
14
CAT. REGEN. LOOP
31D
16
56
58
20
31C
30
31B
50L
54
52
50
30F
30
31A
50L
OFF GAS
46
49
47
44
43
42
FUEL GAS
65
64
40V
40
41
60
61
63
LPG
3
12
2E
C2H4 PRODUCT
1
OLEFIN FEED
2
2L

FIG. 2

FIG. 3


C_2H_4
3D
3B
DISTILLATE
3
GASOLINE SORBENT
3A
3C
HEAVY SORBATE
2F
2E
2C
2D
2A
2G
OLEFINIC FEEDSTOCK
1
2H
2
2B
2K
2J
2L
C_3 + OLEFINS + SORBENT